Atomic and molecular double photoionization calculations using exterior complex scaling

Daniel Horner, Wim Vanroose
Thomas Rescigno, C. William McCurdy
Lawrence Berkeley National Lab, Berkeley, CA

Outline

- **What is the problem?**
  - double photoionization
- **How do we approach this problem?**
  - exterior complex scaling
  - B-Splines
- **Results**
  - helium atom
  - H_2 molecule

Double Photoionization: Introduction

$$\gamma \; + \; \mathrm{A} \; \rightarrow \; \mathrm{A}^{++} + 2e^{-}$$

Double photoionization results in two ejected electrons and plays a key role in many important physical applications. Since a single photon can only interact directly with one electron, the process of double photoionization is controlled entirely by electron correlation. **The details of double photoionization can provide a sensitive test to theoretical methods**.

Research areas and applications in this field range from microelectronics fabrication and plasma physics to radiation damage in biological systems and materials. Our aim is to understand the details and mechanisms of these important processes.

Double Photoionization: Wave equation for double photoionization

A photon interacting with a target atom or molecule, in the weak field limit, is described by the **first order wave equation**,

$$\left(E_0 + \hbar\omega + \frac{1}{2}\nabla^2 - V\right)\Psi^+_{\rm sc} = \mu \cdot \epsilon \; \Phi_0 \ ,$$

where Φ_0 is the initial bound state of the target. For ionization we must have that the **solution** $\Psi^+_{\rm sc}$ **be purely outgoing**. Formally, the asymptotic form of the ionization wave function,

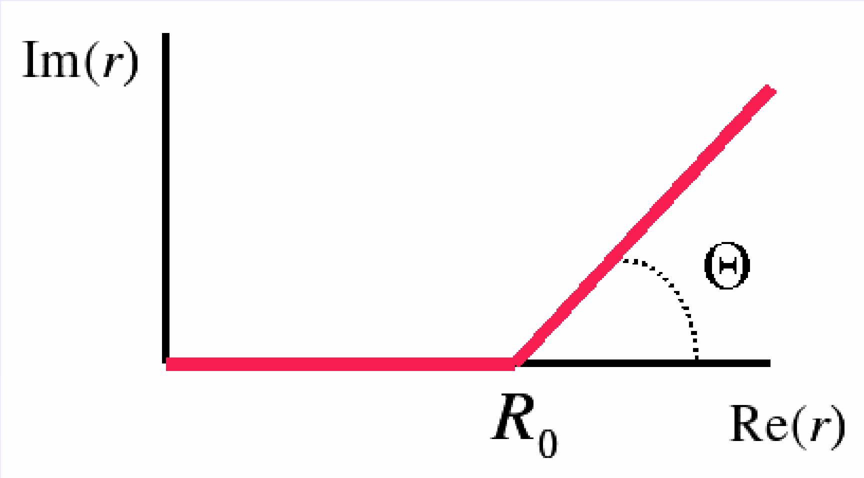
$$\Psi^+_{\rm sc}(\mathbf{r}_1, \mathbf{r}_2) \underset{\rho\to\infty}{\sim} -f(\hat{r}_1, \hat{r}_2, \alpha)\sqrt{\frac{i\kappa^3}{\rho^5}} \exp i \left(\kappa\rho + \frac{\zeta(\hat{r}_1 \cdot \hat{r}_2, \alpha)}{\kappa} \ln(2\kappa\rho)\right)$$

is complicated and is only valid in specific and limited circumstances.

Methods: Exterior complex scaling

Exterior complex scaling (ECS) is a transformation of coordinates which we apply to the radial coordinates of the electrons.

$$R(r) = \begin{cases} r & r < R_0 \\ R_0 + (r - R_0)e^{i\theta} & r \geq R_0 \end{cases}$$



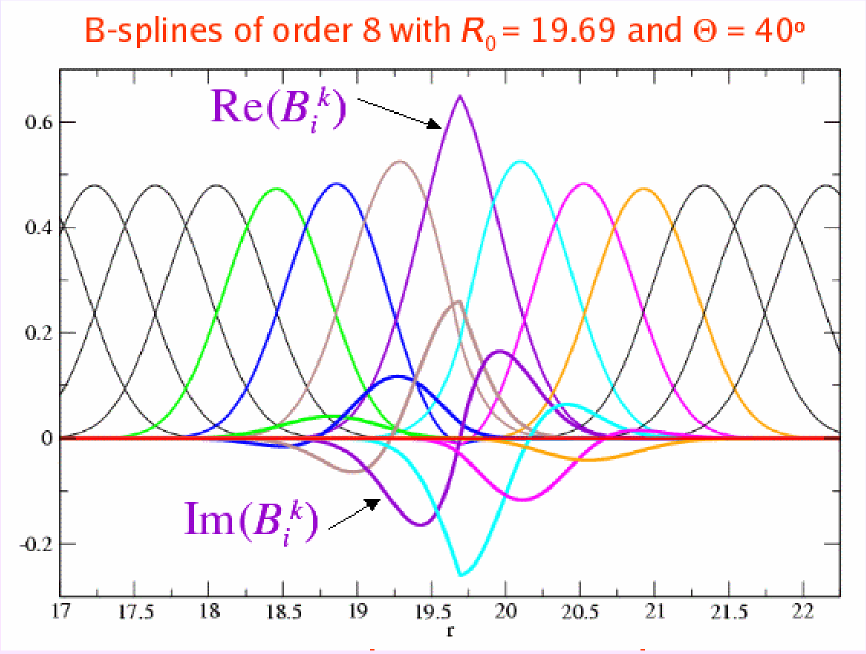
Functions that are purely outgoing decay exponentially on the complex contour. By requiring the solution vanish at a sufficiently large distance along the complex portion of the contour, **ECS enforces the outgoing boundary conditions without making any reference to any specific asymptotic form**.

Methods: B-Splines

ECS requires a coordinate grid and has previously been implemented with finite difference, finite elements, and discrete variable representations (spectral methods). B-Splines are widely used atomic and molecular physics. In combination with ECS, the **B-Spline knot points form the numerical grid** on which we expand the wave functions.

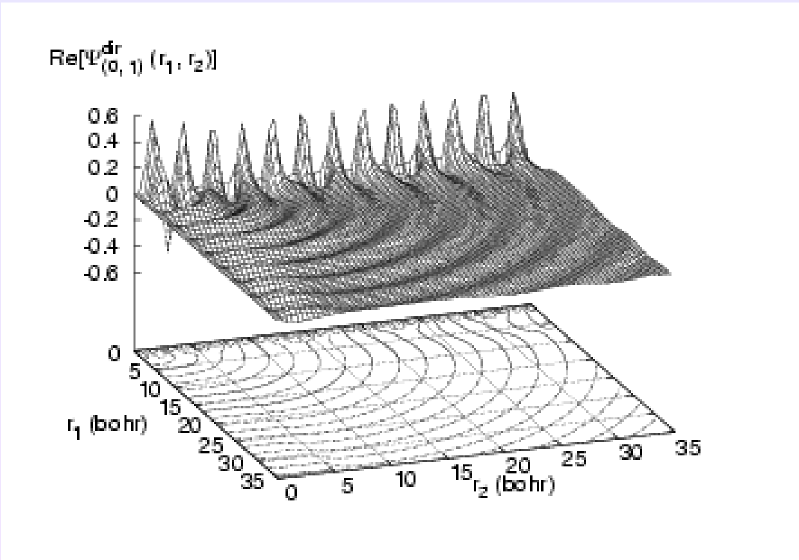
ECS and B-Splines

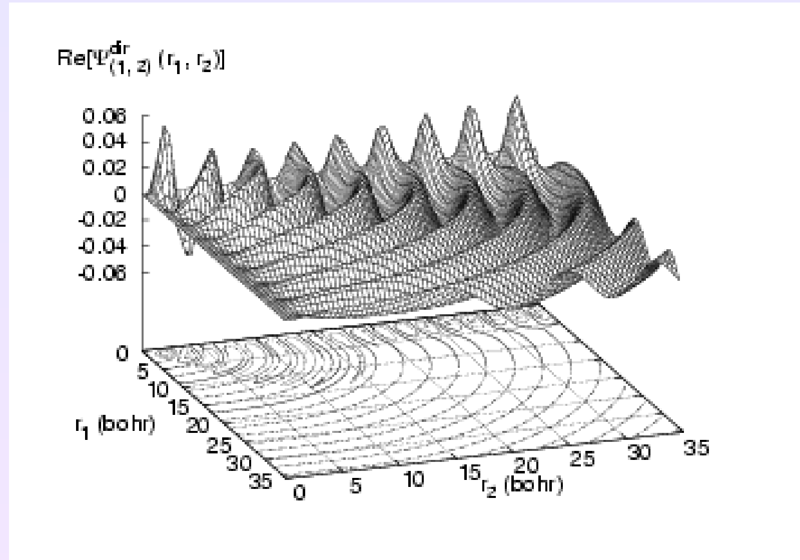
- Place one "knot point" at R_0
- Derivative discontinuity at R_0 from ECS is treated exactly with B-Splines
- Evaluate the B-Spline basis functions on the complex contour $B_i(r) \longrightarrow B_i(R(r))$

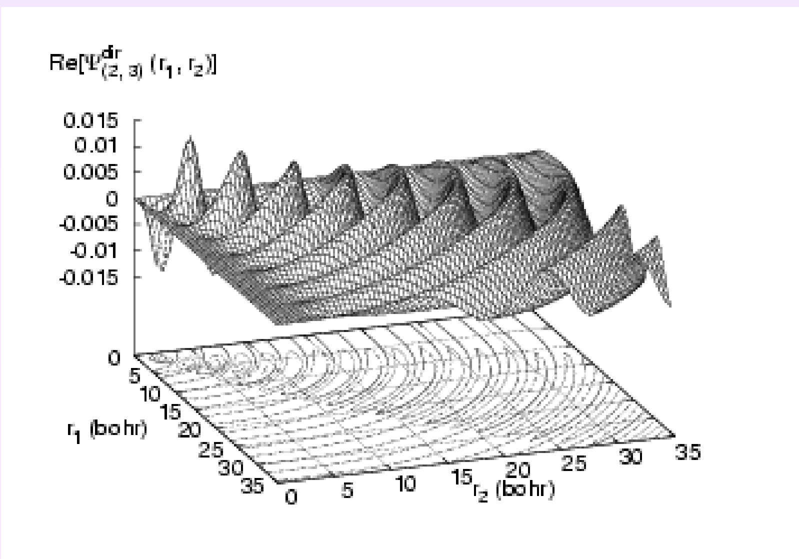


Only the B-Spline basis functions that span the complex turning point R_0 are complex.

Results: Helium double photoionization wave funcions







Real part of direct contribution to the wave function at $20\,\mathrm{eV}$. Plots, clockwise from top-left, are of the $(k_s\,k_p)$, $(k_p\,k_d)$, and $(k_d\,k_f)$ components of the wave function.

Results: Triple differential cross sections

The amplitude for double photoionization is given by

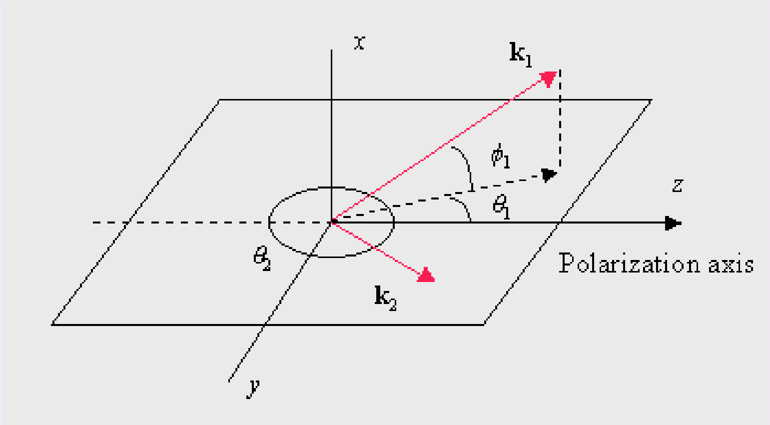
$$f(\mathbf{k}_1,\mathbf{k}_2) = \left\langle \Phi^-(\mathbf{k}_1,\mathbf{r}_1)\Phi^-(\mathbf{k}_2,\mathbf{r}_2)\left|E - T - V_1\right|\Psi_1^+\right\rangle_{R_0} \;;$$

$\Phi^{(-)}(\mathbf{k},\mathbf{r})$ are functions that represent the unbound electrons.

The triple differential cross section (TDCS)

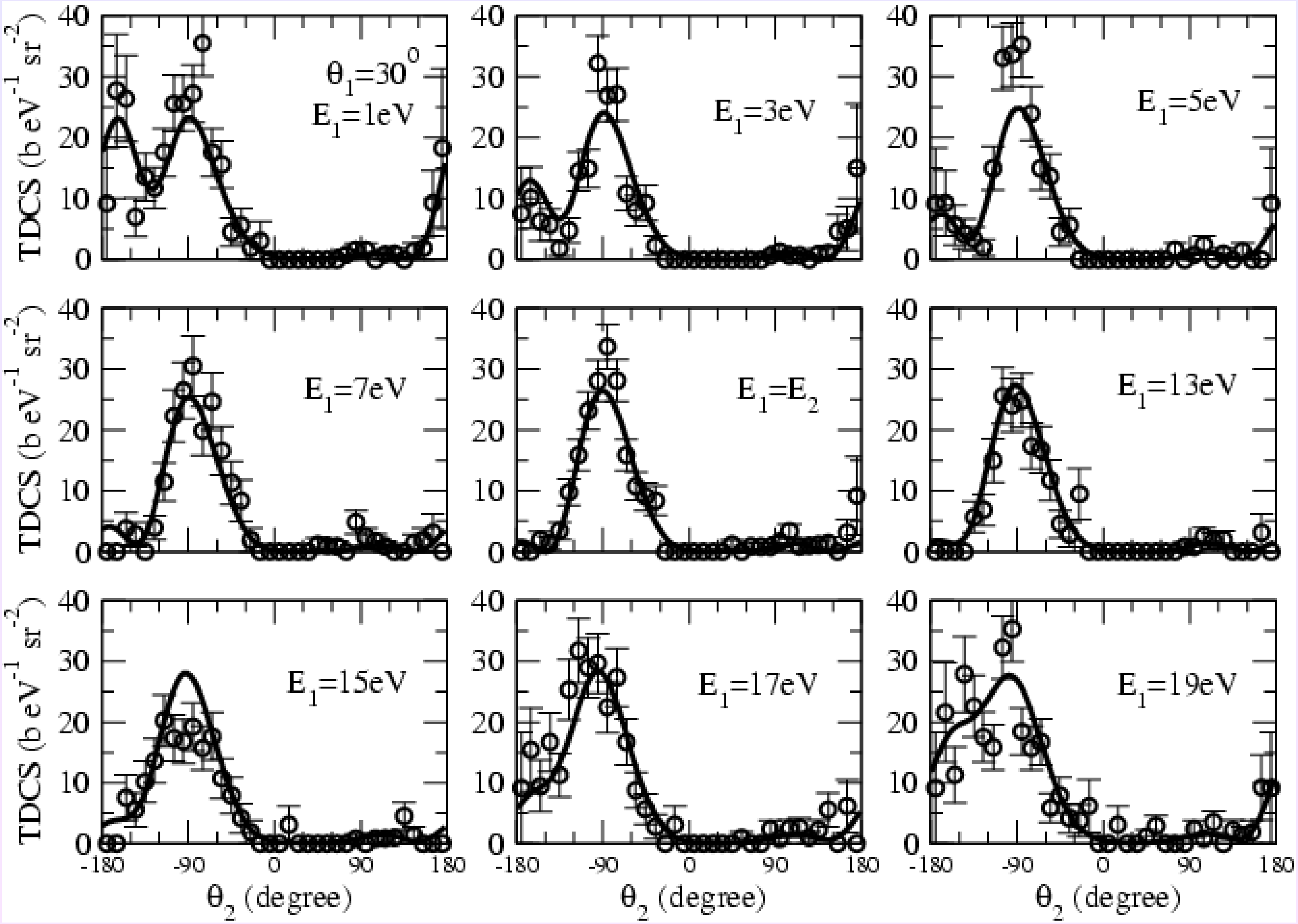
$$\frac{d^3\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{4\pi^2}{\omega c} k_1 k_2 \left|f(\mathbf{k}_1,\mathbf{k}_2)\right|^2$$

is the most detailed measurement of the double photoionization process, as it is a function of the directions of the two ionized electrons and the energy sharing between them.



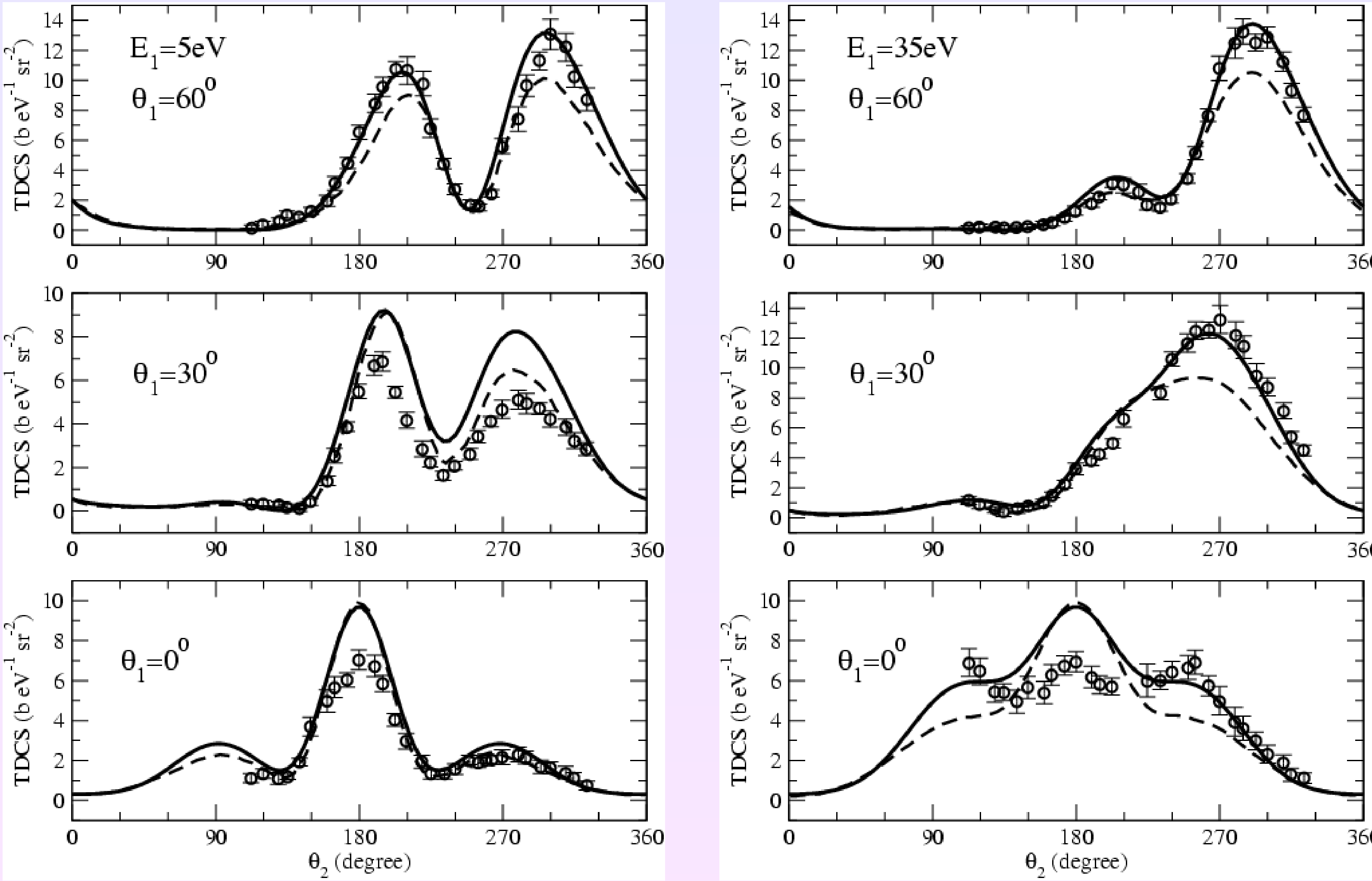
www.lbl.gov/cs/amo_theory

Results: Helium triple differential cross sections I



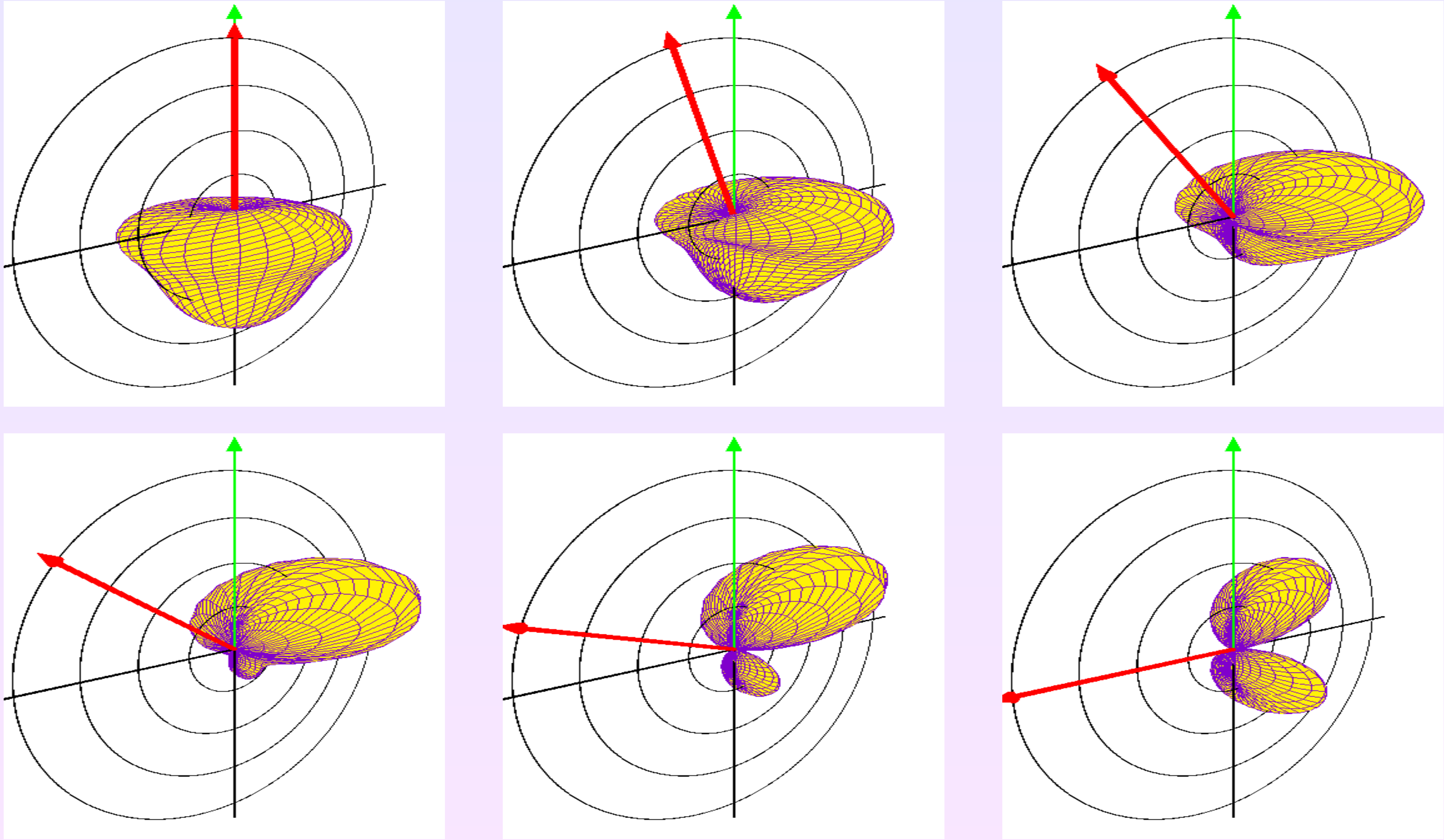
TDCS at 20 eV above threshold for the geometry $\theta_1 = 30^\circ$. Shown are various energy sharings for the given energy E_1. Solid curve: ECS. Circles: experiment by Braüning *et al.* [J. Phys B **31** 5149 (1988)].

Results: Helium triple differential cross sections II



TDCS at 40 eV above threshold complementary energy sharing cases for various θ_1 angles. Solid curves: ECS. Broken curves and circles: CCC calculation and experiment of J. Phys. B **34**, 3193 (2001).

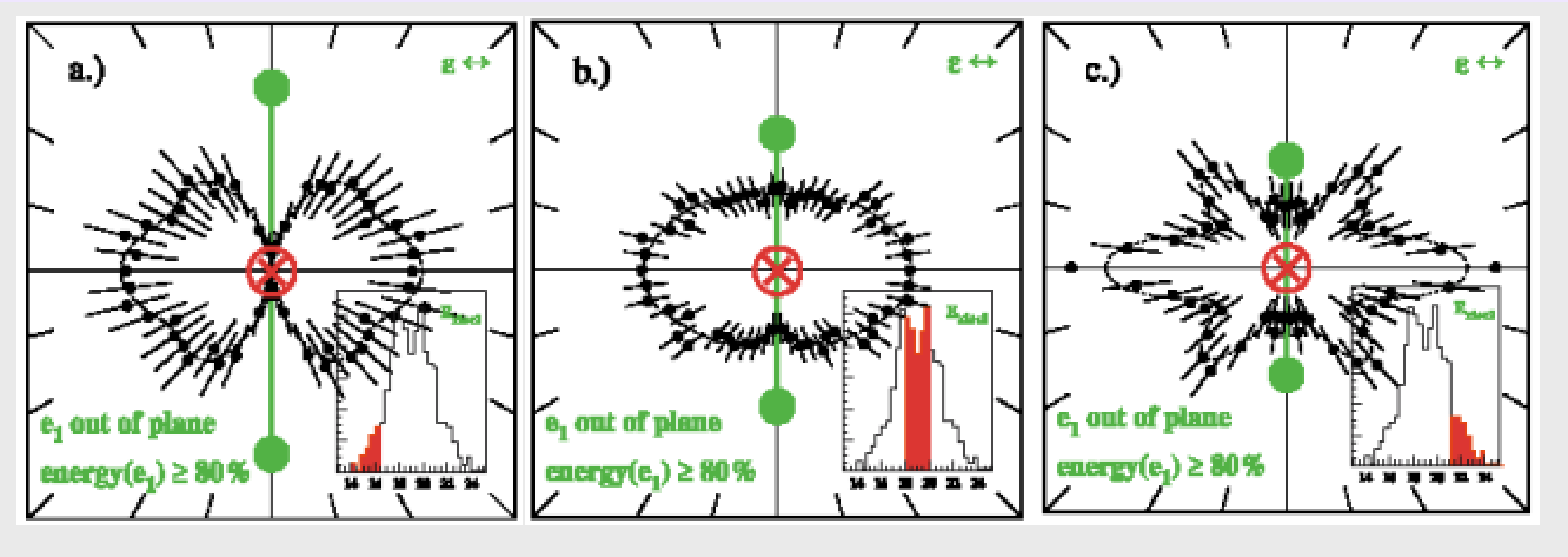
Results: He 3D TDCS surfaces



Three dimensional TDCS plots for photon energy 40 eV above threshold. Green vertical arrow is the photon polarization direction. Red arrow represents the direction of a 35 eV ejected electron, The surface shows the angular ejection distribution of the 5 eV second electron.

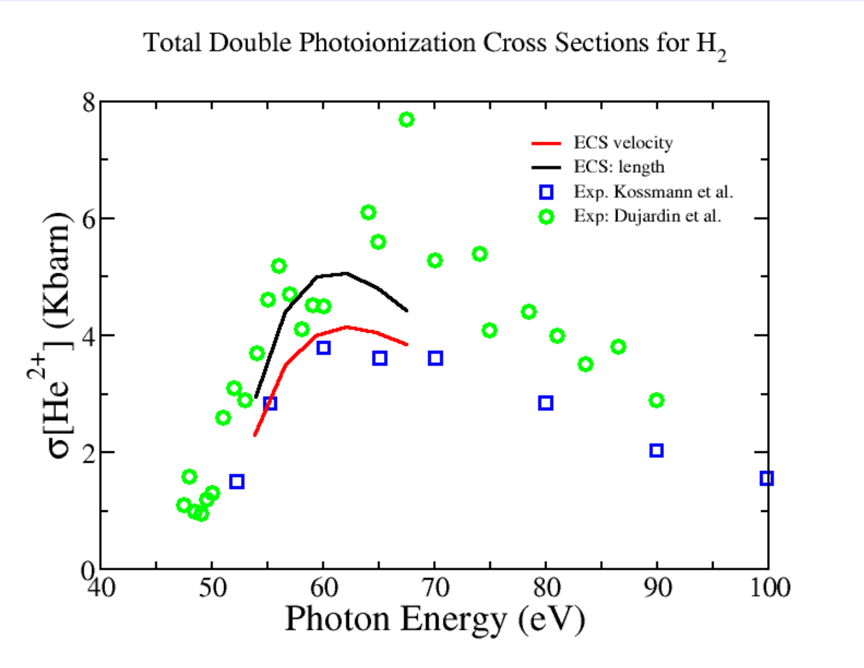
Results: H_2 total double photoionization

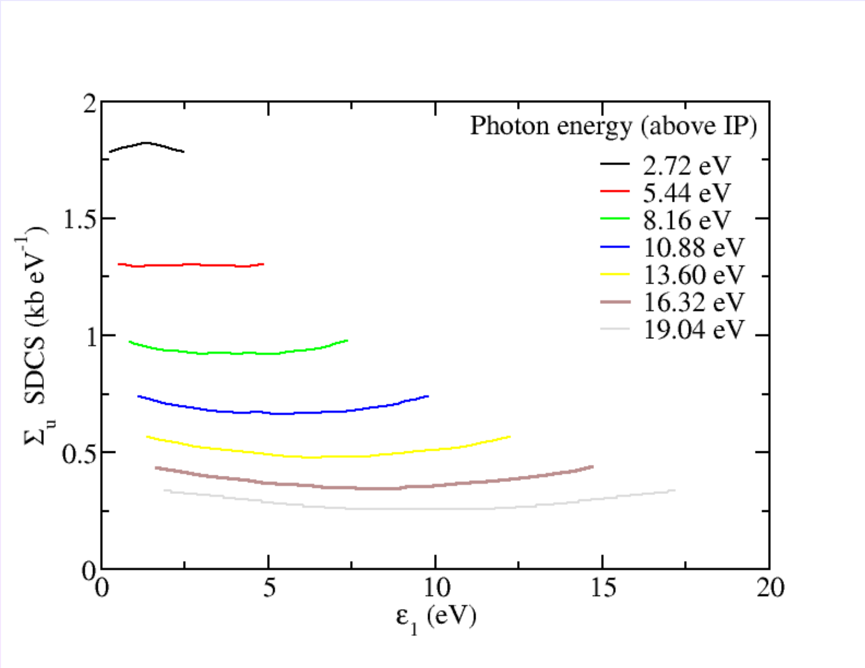
The **non-spherical** nature of molecules gives us additional theoretical challenges as well as additional physics. We must include more terms in our wave function expansion and our cross sections depend on **molecular orientation and bond distance**.



Experimental angular distributions of one electron from D_2 for different bond distances. Other electron coming straight out. Left to right: stretched bond; equilibrium bond distance; compressed bond. [Thorsden Weber: Ph.D Thesis, U. Frankfurt (2003)]

Results: H_2 double photoionization cross sections





Left: H_2 total double photoionization cross sections. Solid curves: ECS results in length (black) and velocity (red) guage. Circles: experiment of Dujardin *et al.*, Phys. Rev. A **35**, 5012 (1987). Squares: experiment of Kossmann *et al.*, Phys. Rev. Lett. **63**, 2040 (1989)

Right: Single differential (energy sharing) cross sections for Σ_u symmetry (bond parallel to the photon polarization) for various photon energies.

Summary

- **Exterior Complex Scaling and B-Splines provide a powerful combination for solving double photoionization problems**
- **Accurate amplitudes and differential cross sections for double photoionization of helium**
- **First fully *ab initio* treatment of molecular double photoionization is underway**